Evidence for time-reversal symmetry breaking in superconducting $PrPt_4Ge_{12}$

A. Maisuradze,[1,*] W. Schnelle,[2] R. Khasanov,[1] R. Gumeniuk,[2] M. Nicklas,[2]
H. Rosner,[2] A. Leithe-Jasper,[2] Yu. Grin,[2] A. Amato,[1] and P. Thalmeier[2]

[1]*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[2]*Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany*

Zero and longitudinal field muon spin rotation (μSR) experiments were performed on the superconductors $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$. In $PrPt_4Ge_{12}$ below T_c a spontaneous magnetization with a temperature variation resembling that of the superfluid density appears. This observation implies time-reversal symmetry (TRS) breaking in $PrPt_4Ge_{12}$ below $T_c = 7.9\,\mathrm{K}$. This remarkably high T_c for an anomalous superconductor and the weak and gradual change of T_c and of the related specific heat anomaly upon La substitution in $La_{1-x}Pr_xPt_4Ge_{12}$ suggests that the TRS breaking is due to orbital degrees of freedom of the Cooper pairs.

PACS numbers: 76.75.+i, 74.70.Dd, 74.25.Ha

I. INTRODUCTION

The large family of filled skutterudite compounds RT_4X_{12} (R = rare-earth, actinides, alkaline-earth, and alkali metals; T = Fe, Ru, Os; X = P, As, Sb) displays an astonishing diversity of physical properties among which superconductivity represents a particularly complex one. Within more than 20 isostructural skutterudites known up to now a perplexing multitude of conventional and unconventional superconducting phases has been observed.[1–5] In large part, the filler cations R which are embedded in the polyanionic $[T_4X_{12}]$ host structure have a significant influence on these properties. Superconducting members of this family containing Pr have attracted considerable interest with $PrOs_4Sb_{12}$ being the most prominent one. While $LaOs_4Sb_{12}$ (critical temperature $T_c = 0.74\,\mathrm{K}$) is found to obey the classical BCS-theory, $PrOs_4Sb_{12}$ ($T_c = 1.85\,\mathrm{K}$) exhibits heavy-fermion behavior and unconventional superconductivity[6–8] with time-reversal symmetry (TRS) breaking.[9,10] Moreover, multiple superconducting phases and order parameters with nodes have been detected.[8] Recent research efforts show that these phenomena depend on a subtle interplay of the crystal electric field (CEF) acting on the Pr^{3+} ion together with the hybridization of the f-shell with the conduction electrons of the host. This is also found, e.g., for the $R[Fe_4P_{12}]$ system, where $LaFe_4P_{12}$ and YFe_4P_{12} are conventional superconductors and isovalent substitution by Pr leads to an antiferro-quadrupolar ground state with heavy electron masses.[6,11,12]

Recently, we investigated the properties of a different family of compounds with a filled skutterudite structure based on platinum and germanium, RPt_4Ge_{12} (R = Sr, Ba, La, Ce, Pr, Nd, Eu).[13] The compounds with Sr and Ba,[13,14] Th,[15] and with La and Pr[13,16] are superconductors. These latter compounds have the highest T_c among the $[Pr_4Ge_{12}]$ skutterudites of 8.3 K and 7.8 K, respectively. In addition to the surprisingly high T_c of $PrPt_4Ge_{12}$ its superconducting energy gap has point nodes, as has been demonstrated by specific heat as well as muon spin rotation measurements down to very low reduced temperatures ($T/T_c \leq 0.005$).[16]

An analysis of the temperature variation of the superfluid density has shown that the data can be well described by three selected gap functions, of which two are compatible with the thermodynamic data.[16] One of the remaining functions, $|\Delta| = \Delta_0|\hat{k}_x - i\hat{k}_y|$, has been favored to describe the *unconventional* superconducting low-field (B) phase of $PrOs_4Sb_{12}$, for which TRS breaking[8–10,17] is observed and has been discussed in connection with spin-triplet pairing.[18] Moreover, the gap-to-T_c ratios Δ_0/k_BT_c of the two Pr superconductors are similar. While these aspects of the superconducting states of $PrPt_4Ge_{12}$ and $PrOs_4Sb_{12}$ are similar, the CEF splitting distinguishes the compounds. Having the same nonmagnetic singlet ground state Γ_1, in $PrOs_4Sb_{12}$ the first excited triplet $\Gamma_4^{(2)}$ ($E/k_B \simeq 7-10\,\mathrm{K}$)[8] strongly hybridizes with the ground state and the conduction electrons, generating the heavy-fermion state. In $PrPt_4Ge_{12}$ the first excited CEF state is a different triplet ($\Gamma_4^{(1)}$ in T_h notation). The Γ_1–$\Gamma_4^{(1)}$ splitting is huge (120–130 K),[13,19,20] allowing for a T_c only little less than for $LaPt_4Ge_{12}$. No heavy-electron states are present at the Fermi surface of $PrPt_4Ge_{12}$, as can be concluded from thermodynamic data.[13]

TRS breaking can lead to the appearance of a small magnetic moment of the superconducting condensate due to spin or orbital degrees of freedom of the Cooper pairs.[21] Muon spin rotation (μSR) successfully detected this field in a number of *unconventional* and *spin-triplet* superconductors.[9,18,22–24] Here, we report on detailed zero magnetic field (ZF) μSR experiments in $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$. The absolute value and the mechanism of ZF muon depolarization above T_c in $PrPt_4Ge_{12}$ are similar to that reported for $PrOs_4Sb_{12}$. Below $T_c = 7.8\,\mathrm{K}$ a spontaneous magnetization resembling the temperature dependence of the superfluid density was observed for $PrPt_4Ge_{12}$. No such anomaly is detected for $LaPt_4Ge_{12}$. The magnitude of this magnetization is of the same order as that reported for $PrOs_4Sb_{12}$ and other superconductors with TRS breaking.[9,22,23] Due to the contrasting behaviors of the La and Pr compound and in order to elucidate the origin of the TRS breaking we synthesized

samples of the solid solution $La_{1-x}Pr_xPt_4Ge_{12}$ and studied the variation of T_c and of the specific heat anomaly.

II. EXPERIMENTAL

The preparation procedures of the $La_{1-x}Pr_xPt_4Ge_{12}$ samples are similar to that described previously.[13] The end member samples have residual resistance ratios $\rho_{300\,\mathrm{K}}/\rho_0 \geq 30$ and the $PrPt_4Ge_{12}$ sample showed crystallites up to 2 mm size. The zero and longitudinal field (ZF & LF) μSR experiments were performed on the DOLLY spectrometer at the πE1 beam line at the Paul Scherrer Institute (Villigen, Switzerland). In addition, a powdered sample of $PrPt_4Ge_{12}$ was measured in ZF on the GPS spectrometer at the πM3 beam line. The samples were cooled in ZF or LF down to 1.5 K and μSR spectra were taken as a function of temperature. During ZF measurements, an active magnetic-field compensation with three orthogonal couples of Helmholtz coils was used in order to reduce the field at the sample to values lower than 3×10^{-6} T. Typical counting statistics were 12×10^6 positron events per each particular data point. Magnetization was measured in a commercial SQUID magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows ZF and LF μSR time spectra for $PrPt_4Ge_{12}$ at 1.5 K and 10 K. The spectra of several histograms were fitted simultaneously. Each histogram is described by the function:

$$N(t) = N_0 \exp(-t/\tau)(1 + AP(t)) + B, \tag{1}$$

where $\tau = 2.197019\,\mu$s is the muon lifetime, N_0 a proportionality coefficient, B the background, A the asymmetry, and $P(t)$ the muon depolarization function. Preliminary fits showed that the ZF muon depolarization is well described by a Kubo-Toyabe depolarization function reflecting a static Voigt field distribution, i.e. describing two mechanisms for the profile, one producing a Gaussian distribution and one producing a Lorentzian distribution.

The zero and longitudinal field μSR depolarization functions for the static Voigt field distribution were calculated using the general formula derived by R. Kubo, (Eq. 21 of Ref. 25). For Voigt-like functions this equation can be reformulated as follows:

$$P_G(t) = 1 - \frac{2Q'(t)}{\omega_0^2 t}[\cos\omega_0 t - j_0(\omega_0 t)] - 2\int_0^t \frac{Q'(s)}{s}\frac{j_0'(\omega_0 s)}{\omega_0} ds. \tag{2}$$

Here, $j_0(x) = \sin(x)/x$, $\omega_0 = \gamma_\mu B$ is the Larmor frequency corresponding to the applied longitudinal field B. For the Voigt function $Q(t) = \exp(-\frac{1}{2}\sigma^2 t^2 - \lambda t)$, where σ^2/γ_μ^2 is the second moment of the Gaussian distribution and λ/γ_μ is the half-width at half-maximum

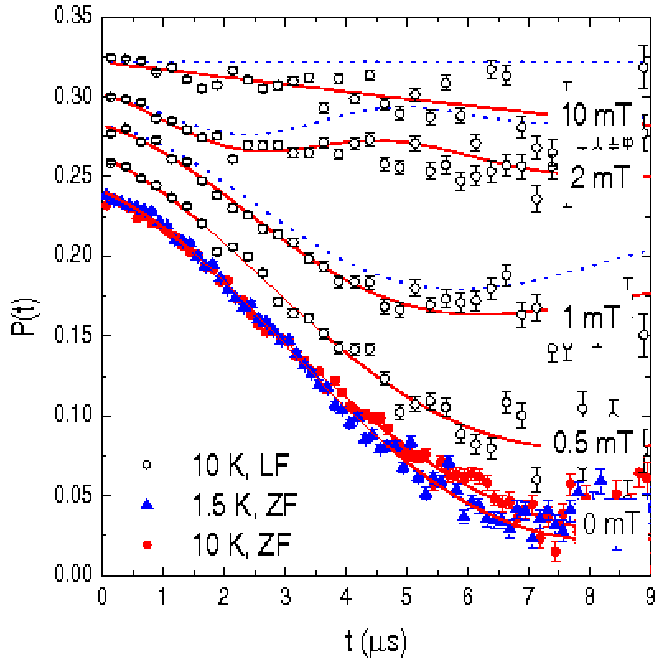

FIG. 1: (Color online) Zero field μSR time spectra at 1.5 K (▲) and 10 K (●) for $PrPt_4Ge_{12}$. The corresponding solid red lines are fits to the data according to Eq. (5). (○) Spectra measured with longitudinal fields (LF) of 0.5 mT, 1 mT, 2 mT and 10 mT at 10 K and corresponding fit with Eq. 5 (the solid red lines). The blue dashed lines are simulation of the spectra assuming only the static field distribution (i.e. $\lambda_d = 0$). For better visualization each LF spectrum is shifted by 0.02 units.

of the Lorentzian distribution, and finally the prime denotes the derivative.[25] In the limit of $\omega_0 \to 0$ (i.e. in the ZF situation), Eq. 2 converges to the "golden formula" of Kubo:[26]

$$P_{G,ZF}(t) = \frac{1}{3} + \frac{2}{3}[Q(t) + Q'(t)t], \tag{3}$$

and for the case of $Q(t) = \exp(-\frac{1}{2}\sigma^2 t^2 - \lambda t)$ one finally gets the equation:

$$P_{G,ZF,V}(t) = \frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2 - \lambda t)\exp\left(-\frac{1}{2}\sigma^2 t^2 - \lambda t\right). \tag{4}$$

Actually, a closer look at the data indicates that the ZF and LF data are best fitted using the depolarization function:

$$P(t) = P_G(t)\exp(-\lambda_d t), \tag{5}$$

where $\lambda_d \simeq 0.020\,\mu s^{-1}$ (which is practically temperature independent) is a dynamical muon depolarization which does not decouple up to fields of 20 mT. Such dynamical depolarization is best seen in LF experiments. In Fig. 1, the fits obtained with Eq. 5 are shown with the solid red curves. The best fit to the data is obtained with field independent parameters $\sigma = 0.173\,\mu s^{-1}$, $\lambda =$

$0.029\,\mu s^{-1}$, and $\lambda_d = 0.020\,\mu s^{-1}$. The total asymmetry $A = 0.242$ was fixed during the fitting procedure. The small dynamic contribution λ_d to the relaxation is obvious only when comparing the LF spectra with the depolarization curves calculated for the case of a static only field distribution (see the blue dotted curves in Fig. 1). Note that for such small values of λ and λ_d, as in the present case, these parameters are strongly correlated in the ZF spectra. However, LF experiments allow us to disentangle this correlation. Zero and longitudinal field experiments suggest the presence of static muon depolarization predominantly from nuclear moments of the Pr, Pt, or Ge isotopes. Note that usually for a depolarization due to nuclear moments, one assumes a Gaussian field-distribution (i.e. a situation with $\lambda = 0$). However, a pure Gaussian field distribution is an approximation and does not take into account, for example, the presence of different isotopes with different nuclear moments (as for Pt and Ge). It is therefore likely that the field distribution due to nuclear moments is not purely Gaussian in our case. Note also that the main conclusions concerning the temperature dependence of the muon depolarization (see below) do not depend on the exact static field distribution assumed. Decoupling of this static field is well described with the general expression given in Eq. 5.[25] The small dynamic contribution λ_d which does not decouple up to fields of 20 mT is presumably due to some additional spin-lattice relaxation mechanisms.

When studying the temperature dependence of the parameters σ and λ, we first noticed that λ is practically independent of temperature. In a second step, λ was fixed to its average value $0.029\,\mu s^{-1}$ and solely σ was kept free. Figure 2 presents $\sigma(T)$ recorded in ZF for $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$, measured on two different spectrometers. For the Pr compound, above $T_c = 7.8$ K σ is independent of temperature, as expected for depolarization due to nuclear moments.

However below T_c one can observe a clear increase of the muon relaxation rate with decreasing temperature. Just below T_c the data systematically decrease below the normal-state level showing a small dip. The rise of σ starts only below ≈ 6.5 K. There is no indication for a phase transition at this temperature from other measurements as, e.g., specific heat or the superfluid density.[13,16]

The corresponding ZF depolarization rates $\sigma(T)$ for $LaPt_4Ge_{12}$ with $T_c = 8.3$ K (obtained via Eq. 5 with $\lambda = \lambda_d = 0$ and free parameter σ) are small and temperature-independent (see Fig. 2).[27] No anomaly is resolved at $T_c = 8.3$ K. σ for $LaPt_4Ge_{12}$ is substantially smaller than in $PrPt_4Ge_{12}$, indicating that in $PrPt_4Ge_{12}$ the dominant part of the relaxation is due to the presence of ^{141}Pr nuclei.

A similarly strong (nearly the same value of σ) hyperfine-enhanced nuclear muon depolarization was observed in the isostructural $PrOs_{4-x}Ru_xSb_{12}$ compounds.[28] The authors explain the relaxation by a Van-Vleck-like admixture of magnetic excited CEF states into the nonmagnetic Γ_1 ground state of Pr^{3+} by the nuclear hyperfine coupling. This hybridization strongly increases the strength of the interactions between the ^{141}Pr nuclear spins and the muon spins as well as within the ^{141}Pr nuclear spin system.[29] Lei Shu *et al.* observe that this relaxation is *dynamic* due to the relatively low energy ($E/k_B \simeq 7$–10 K for $x = 0$) of the first exited CEF level $\Gamma_4^{(2)}$ of Pr^{3+} with a spin-spin correlation time $\tau_c \simeq 0.2$–$0.6\ \mu s^{-1}$. For $PrPt_4Ge_{12}$, the first exited CEF level $\Gamma_4^{(1)}$ is found at $E/k_B \simeq 120$–130 K,[13,19,20] in agreement with our observation of a quasi-static nuclear magnetism of Pr. The very small population of all exited CEF states at $T \simeq T_c = 7.8$ K is the reason for this behavior and the negligible Cooper-pair breaking in $PrPt_4Ge_{12}$. The origin of the additional dynamic relaxation λ_d in the present case is unknown. To reduce the magnitude of λ_d in LF the LF Larmor precession frequency should exceed the characteristic fluctuations of magnetic field probed in the sample.[30] Since it does not decouple up to 20 mT one estimates the characteristic fluctuation frequency larger than $\nu > 2\pi\gamma_\mu \cdot 0.02 = 17$ MHz.

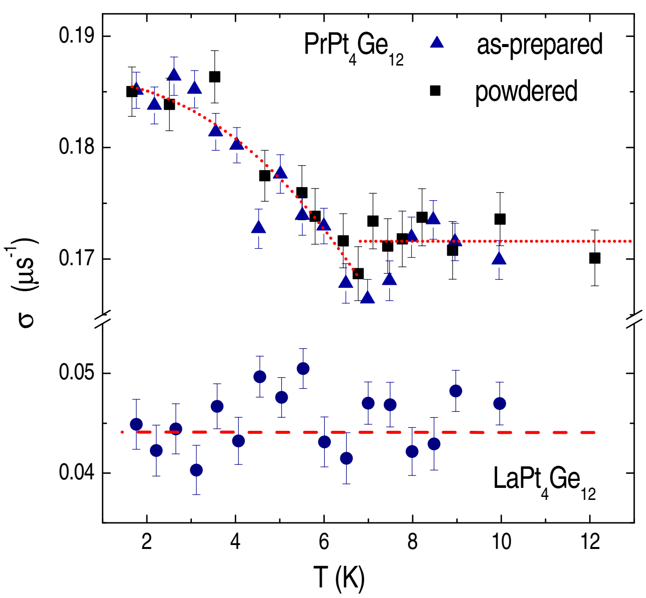

FIG. 2: (Color online) Temperature dependence of the muon depolarization rate σ in "as-prepared" (▲) and powdered (■) samples of $PrPt_4Ge_{12}$ and in "as-prepared" $LaPt_4Ge_{12}$ (•) as obtained by Eq. (5). The lines are guides to the eye (see text).

Figure 3 shows the susceptibility measurements for the series of $La_{1-x}Pr_xPt_4Ge_{12}$ samples. The magnetic susceptibility $\chi(T)$ of the $La_{1-x}Pr_xPt_4Ge_{12}$ samples becomes temperature-independent below ~20 K (see Fig. 3) and the amplitude simply scales with the Pr content x, as expected for a single-ion CEF effect. No detectable Curie-like contributions indicating localized magnetic impurities (e.g. Pr^{3+} ions on different crystallographic sites or in secondary phases) are observed. The inset of Fig. 3 displays the dependence of T_c on x in $La_{1-x}Pr_xPt_4Ge_{12}$. This dependence is weak and the small sagging of the curve below the linear relationship may be due to the

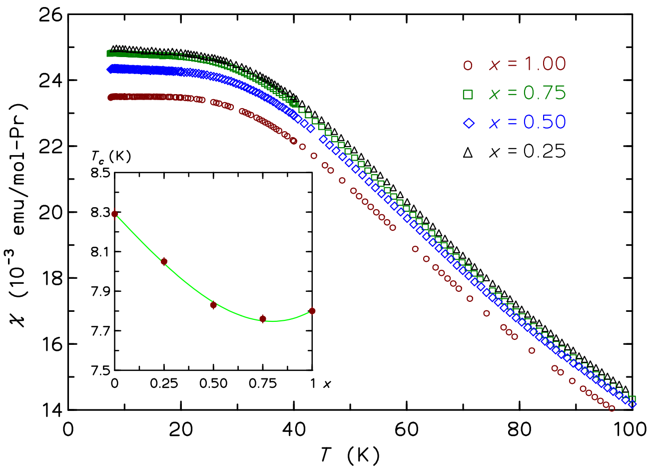

FIG. 3: (Color online) Magnetic susceptibility of Pr_xLa_{1-x}-Pt_4Ge_{12} samples in $\mu_0 H = 0.1\,T$. The inset shows the superconducting T_c ($\mu_0 H = 2\,mT$) *vs* the nominal Pr-content x.

weak crystallographic disorder introduced by the statistical occupation of the $2a$ site. Specific heat data (not shown) reveal that also the size of the specific heat jump $\delta c_p/T_c$ at T_c varies linearly with the Pr content x. This is in contrast to the observations in the series $La_{1-x}Pr_xOs_4Sb_{12}$ where $\delta c_p/T_c$ shows a strongly non-linear variation with x.[8] For the substitution series $PrOs_{4-x}Ru_xSb_{12}$ even a strong depression of T_c well below that of both end members is observed.[8,28,31]

In the ZF μSR data (Fig. 2) it can be seen that for $PrPt_4Ge_{12}$ the data show the presence of an additional depolarization below T_c. In addition, our data seems to reveal a small dip of $\sigma(T)$ just below T_c. At the moment we do not have an explanation for this dip. Most plausible would be the presence of diluted magnetic centers separated on distances of order of the magnetic penetration depth $\Lambda \simeq 120\,nm$. In such a case, a reduction of σ is expected due to screening of the magnetic field by the superfluid condensate. The required concentration of such impurities would be of the order of $\sim 0.01 - 0.1\%$ [from $\sigma(T > T_c)$]. Clearly, such impurities are not present in our samples as can be concluded from the absence of an upturn in the magnetic susceptibilities toward low temperatures (see Fig. 3). Another possibility for this dip could be a coupling of Pr nuclei with free carriers. Below T_c the density of states at the Fermi level N_F drops. Hence, in case of a Korringa-like coupling it is expected that the muon relaxation will drop $\propto N_F^2$. However, the observation of quasi-static magnetism of the Pr nuclei contradicts this assumption.

Beyond the possible observation of this small dip, the main observation is the *increase* of σ upon lowering the temperature below T_c. Such an increase cannot be explained by a Pr–Pr RKKY-coupling, since it would reduce the muon depolarization below T_c ($\propto N_F^n$), in contrast to our observation. The influence of external fields can be excluded, since true zero field was controlled with high precision and, moreover, the Meissner effect automatically shields any fields in the superconducting state. Note, only for the heavy-fermion superconductor $PrOs_4Sb_{12}$ a similar spontaneous magnetization was detected to appear below T_c[9] whereas there is no change of σ in $PrRu_4Sb_{12}$ at T_c.[32] In both of these samples a nearly similar muon depolarization was observed above T_c. The electronic specific heat coefficient γ and N_F are small for $PrPt_4Ge_{12}$.[13,16] In addition, our measurements of two different samples of $PrPt_4Ge_{12}$ ("as-prepared" and powdered) on two different spectrometers with the same result and no anomaly at T_c for $LaPt_4Ge_{12}$ strongly supports that the enhanced depolarization below T_c is an intrinsic property of the superconducting state of $PrPt_4Ge_{12}$.

The enhanced muon depolarization below T_c gives evidence of *time-reversal symmetry* (TRS) breaking in $PrPt_4Ge_{12}$. TRS breaking can be realized for *spin-* or *orbital* multi-component (vector-) order parameters that may have an internal phase degree of freedom between the components.[21] An example is the chiral p-wave triplet state proposed for Sr_2RuO_4[23] and the E_{2u} triplet state for UPt_3.[33,34] Triplet pairing has been proposed – and heavily debated – for $PrOs_4Sb_{12}$.[17,18,35] For $PrPt_4Ge_{12}$ we recently reported[16] that the superfluid density fits well to the expectations of a chiral p-wave form of the gap function $|\Delta| = \Delta_0|k_x \pm ik_y|$ with a gap-to-T_c ratio $\Delta_0/T_c = 2.6$ similar to that of $PrOs_4Sb_{12}$.[8,16] Most interestingly, the T_c of $PrPt_4Ge_{12}$ is larger than that of other proposed *spin-triplet* superconductors which have T_c values $< 2.7\,K$.[9,22–24]

For $LaPt_4Ge_{12}$ we observe no indications for (or an unresolvably small) TRS breaking. Unfortunately, our investigations of the gap symmetry are inconclusive at the moment, however a nodeless gap and spin-singlet pairing has been concluded from NMR relaxation data for $LaPt_4Ge_{12}$.[19] The weak variation of T_c and of $\delta c_p/T_c$ with the Pr-content x in $La_{1-x}Pr_xPt_4Ge_{12}$ indicates that the order parameters of the end members are compatible and not separated by a first-order phase transition. Thus, it is plausible that $PrPt_4Ge_{12}$ is also a *spin-singlet* superconductor. In this case, the observation of TRS breaking in the condensate requires that the gap function belongs to a complex *orbitally* degenerate representation leading to an internal orbital moment of the Cooper pairs. In such a state supercurrents are induced around nonmagnetic impurities which in turn generate a condensate magnetic moment density with a spatial extension of the order of the coherence length ξ.[36] Such a complex spin-singlet state of T_g symmetry with point nodes along the cubic axes has actually been proposed in Ref. 37 to explain the TRS breaking in $PrOs_4Sb_{12}$ and as an alternative to the spin-triplet model. The orbital moment of the Cooper pairs may vary and in this way the seemingly conflicting observations of a TRS broken state for $PrPt_4Ge_{12}$ and of no visible TRS breaking for the La compound as well as a continuous changeover in

$La_{1-x}Pr_xPt_4Ge_{12}$ may appear.

IV. CONCLUSIONS

To conclude, zero field μSR measurements on $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$ showed that the dominant contribution for the muon relaxation comes from the Pr nuclei. Below T_c in $PrPt_4Ge_{12}$ we observe an additional muon depolarization with a temperature variation resembling that of the superfluid density while no anomalous effect was seen for $LaPt_4Ge_{12}$. This observation indicates TRS breaking in the superconducting state of $PrPt_4Ge_{12}$ with an extraordinary high T_c.[21] We have argued that the origin of the TRS breaking is the unconventional multi-component nature of the order parameter. From the present experiments no definite conclusion can be made whether this is due to the spin or orbital degeneracy of the Cooper pairs. The T_c of 7.8 K for $PrPt_4Ge_{12}$ seems to be rather high for spin-triplet pairing. In the series $La_{1-x}Pr_xPt_4Ge_{12}$ the T_c as well as the size of the related specific heat anomaly vary almost linearly with the Pr content x. Together with the absence of TRS breaking for $LaPt_4Ge_{12}$ this renders a spin-triplet Cooper pairing for these compounds, including $PrPr_4Ge_{12}$, unlikely, since one would expect strong effects for incompatible superconducting order parameters. Due to the high tetrahedral symmetry, orbital degeneracies are present which allow for a complex spin-singlet gap function with an internal phase. Such a kind of pairing with orbital degeneracy also breaks TRS and may lead to a condensate with a magnetic moment density.

Part of this work was performed at the Swiss Muon Source (SμS), Paul Scherrer Institute (PSI, Switzerland).

* Electronic address: alexander.maisuradze@psi.ch

1 G. P. Meisner, Physica B+C (Amsterdam) **108**, 763 (1981). L. E. Delong and G. P. Meisner, Solid State Commun. **53**, 119 (1985).

2 T. Uchiumi, I. Shirotani, Ch. Sekine, S. Todo, T. Yagi, Y. Nakazawa, and K. Kanoda, J. Phys. Chem. Solids **60**, 689 (1999).

3 E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506(R) (2002).

4 I. Shirotani, Y. Shimaya, K. Kihou, C. Sekine, N. Takeda, M. Ishikawa, and T. Yagi, J. Phys.: Condens. Matter **15**, s2201 (2003).

5 I. Shirotani, S. Sato, C. Sekine, K. Takeda, I. Inagawa, and T. Yagi, J. Phys.: Condens. Matter **17**, 7353 (2005).

6 H. Sugawara, T. D. Matsuda, K. Abe, Y. Aoki, H. Sato, S. Nojiri, Y. Inada, R. Settai, and Y. Onuki, Phys. Rev. B **66**, 134411 (2002).

7 D. Parker and P. Thalmeier, Phys. Rev. B **77**, 184503 (2008).

8 M.B. Maple, Z. Henkie, W.M. Yuhasz, P.-C. Ho, T. Yanagisawa, T.A. Sayles, N.P. Butch, J.R. Jeffries, and A. Pietraszko, J. Magn. Magn. Mater. **310**, 182 (2007). M. B. Maple, N. A. Frederick, P.-C. Ho, W. M. Yuhasz, and T. Yanagisawa, J. Supercond. Novel Magn. **19**, 299 (2006).

9 Y. Aoki *et al.*, Phys. Rev. Lett. **91**, 067003 (2003).

10 Elbert E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. B **69**, 180509(R) (2004).

11 Y. Nakai, K. Ishida, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Japan **74**, 7353 (2005).

12 K. Magishi, T. Saito, K. Koyama, I. Shirotani, Y. Shimaya, K. Kihou, Ch. Sekine, N. Takeda, M. Ishikawa, and T. Yagi, Physica B (Amsterdam) **359-361**, 883 (2005).

13 R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, and Yu. Grin, Phys. Rev. Lett. **100**, 017002 (2008).

14 E. Bauer *et al.*, Phys. Rev. Lett. **99**, 217001 (2007).

15 D. Kaczorowski and V. H. Tran, Phys. Rev. B **77**, 180504(R) (2008).

16 A. Maisuradze, M. Nicklas, R. Gumeniuk, C. Baines, W. Schnelle, H. Rosner, A. Leithe-Jasper, Yu. Grin, and R. Khasanov, Phys. Rev. Lett. **103**, 147002 (2009).

17 Elbert E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. Lett. **91**, 247003 (2003).

18 W. Higemoto, S. R. Saha, A. Koda, K. Ohishi, R. Kadono, Y. Aoki, H. Sugawara, and H. Sato, Phys. Rev. B **75**, 020510(R) (2007).

19 M. Toda, H Sugawara, K. Magishi, T. Saito, K. Koyama, Y. Aoki, and H. Sato, J. Phys. Soc. Japan **77**, 124702 (2008).

20 E. A. Goremychkin, D. T. Adroja, A. D. Hillier, R. Osborn, B. D. Rainford, and K. A. McEwen, Abstract, Int. Conf. Magnetism, Karlsruhe, 2009, unpublished.

21 M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).

22 R. H. Heffner, J. L. Smith, J. O. Willis, P. Birrer, C. Baines, F. N. Gygax, B. Hitti, E. Lippelt, H. R. Ott, A. Schenck, and D. E. MacLaughlin, Phys. Rev. Lett. **65**, 2816 (1990).

23 G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist, Nature (London) **394**, 558 (1998).

24 A.D. Hillier, J. Quintanilla, and R. Cywinski, Phys. Rev. Lett. **102**, 117007 (2009).

25 R. Kubo, Hyperfine Int. **8**, 731 (1981).

26 R. Kubo, Hyperfine Int. **104**, 3 (1997).

27 The fit with $\sigma = 0$ and free λ is slightly worse and gives also a temperature-independent relaxation.

28 L. Shu *et al.*, Phys. Rev. B **76**, 014527 (2007).

29 B. Bleaney, Physica (Utrecht) **69**, 317 (1973).

30 Y.J. Uemura, T. Yamazaki, D.R. Rarshman, M. Senba, and E.J. Ansaldo, Phys. Rev. B **31**, 546 (1985).

31 N. A. Frederick, T. D. Do, P.-C. Ho, N. P. Butch, V. S. Zapf, and M. B. Maple, Phys. Rev. B *69*, 024523 (2004).

32 D. T. Adroja, A. D. Hillier, J.-G. Park, E. A. Goremychkin, K. A. McEwen, N. Takeda, R. Osborn, B. D. Rainford, and R. M. Ibberson, Phys. Rev. B **72**, 184503 (2005).

33 P. Thalmeier and G. Zwicknagl, Handbook of the Physics and Chemistry of Rare-Earth, Ed. K. A. Gschneidner Jr., J.-C. G. Bünzli, and V. K. Pecharsky, Elsevier, Amsterdam, 2005, **34**, 135–287.

34 P. Dalmas de Réotier *et al.*, Physica B (Amsterdam) **289–290**, 10 (2000).

[35] K. Maki, S. Haas, D. Parker, H. Won, K. Izawa, and Y. Matsuda, Europhys. Lett. **68**, 720 (2004).
[36] C. H. Choi and P. Muzikar, Phys. Rev. B **39**, 9644 (1989).
[37] I. A. Sergienko and S. H. Curnoe, Phys. Rev. B **70**, 144522 (2004).